International Journal of Psychosocial Rehabilitation, Vol. 24, Issue 04, 2020
ISSN: 1475-7192

Preparation and Identification of New Azo ligand [(E)-3-((4,5-Diphenyl-1-Imidazole-2-yl) Diazenyl) Benzene Sulfonic Acid and Some of its Chelate Complexes

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Abstract--- *This paper included preparation of ligand azo new which is derivative from 4,5-di phenyl imidazole. It also included the preparation of metal complexes for ions of Co(II), Ni(II),Cu(II),Zn(II),Cd(II) which is derivative from the new ligand. The ligand and metal complexes has been synthesized by FTIR, UV-Vis,1HNMR and mass spectrum, as the complexes have been synthesized by magnetic susceptibility. As result has proven that the prepared complexes have magnetic determination which are compatible with the octahedral shapes and the results of molar conductivity for the complexes that there is no ionic property for the complexes and based on these results. Octahedral shape has been suggested for all prepared complexes.*

Keywords--- *New Ligand, Metal Complexes, FTIR.*

I. INTRODUCTION

The organic ligands have been characterized by many advantages and have made them used in the field of academic chemistry and especially applied (1).It has proved its ability after being used as precipitation in the field of analytical chemistry (2) because it has high molecular weights as well as their solubility in many organic solvents on the on hand and the fact that it is very low in water on the other hand many have been used in the quantitative estimation of metal ions many of these compounds were characterized by bright colors in the visible rang of the spectrum because they include in their chemical composition some groups of color- bearing such as (C=N- , N=N-, -NO2) etc. Sometimes it includes sophisticated color groups such as (-OH, -Br, -SH, -NH2) etc. The presence of the groups mentioned in the chemical composition of the ligand to the emergence of color and may acquire the character of selectivity and this is a desirable feature of many researchers in the field of inorganic chemistry they have become the subject of interesting the preparation of the complexes (3). The studies also showed the important role of the azo compounds in many industrial (4) and agricultural fields (5) as well as their impact on the biological fields (6). It was so introduced as a ligand in the field of inorganic chemistry in the case of obtaining metal complexes for transitional or representative ions (7).

II. EXPERIMENTAL

In this research, chemicals with a high degree of purity were used. The devices used can be described in physical measurements and spectral complexes. Used in the diagnosis of ligand ant its metal complexes using a spectrometer (Shimadzu FTIR 8400 spectrophotometer). The melting point of the ligand and its metal complexes were also

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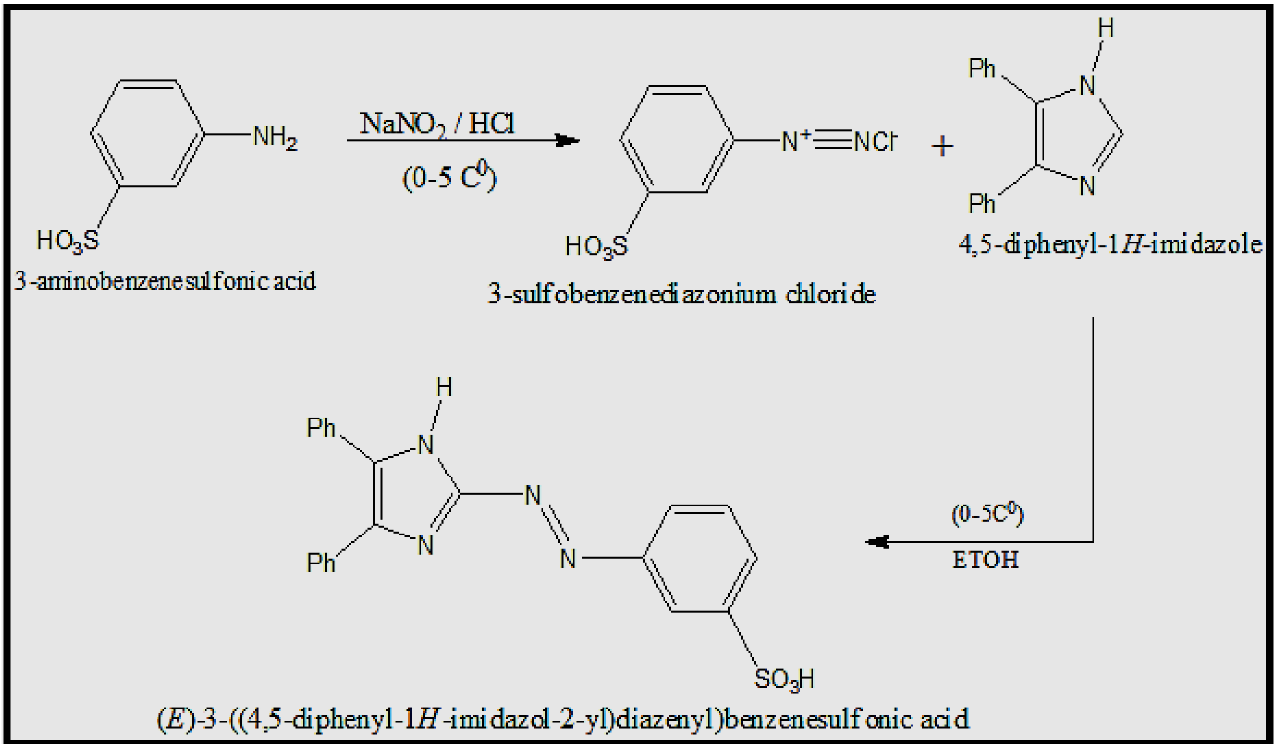
DOI: 10.37200/IJPR/V24I4/PR2020446
Received: 12 Mar 2020 | Revised: 25 Mar 2020 | Accepted: 10 Apr 2020

measured using a device Stuart melting point (SPMSP). The electronic spectra of the ligand and the complexes were recorded using an ultraviolet spectrometer (Shimadzu 1700) within range (200-800 nm) dissolve in ethanol using quartz cell. The molecular conductivity measurements were recorded for the complexes at 25 ± 2 C̊ for solution (1×10-3) of the sample in ethanol using a device (Digital conductivity meter Alpha -800). The 1HNMR spectrum has been determined for ligand only by advice (Bruker 400 MHz). The mass spectrometer was also recorded by advice (MSD Direct Probe).

Preparation of Ligand

The ligand was prepared by dissolving (0.005ml), (0.865 gm) from 3- amino sulfonic acid in mixture of (2 ml of hydrochloric and 20 ml of distilled water) where the mixture was cooled to (0C̊). The add a (0.005 ml), (0.345 gm) solution of sodium nitrite, dissolved in (10 ml) of distilled water droplet of stirring and non- high temperature then leave the solution to settle down and the add the diazonium solution resulting in drop by drop with continuous stirring and cooling in to a (0.005ml), (1.1 gm) solution of dissolved 4,5-diphenyl imidazole in (100ml) of ethanol alcohol. Then add (1gm) of sodium hydroxide dissolved in ethanol was observed the emergence of yellow crystals leaving the solution to the second day and added to it diluted hydrochloric acid to neutralize the solution where an orange deposition was observed after the precipitation was filtered and washed with distilled water to dispose of sodium chloride. The precipitate was dried and reconstituted using absolute ethanol and the melting point was obtained (303-305 C̊). The Scheme (1) shows how to prepare.



Scheme 1: Synthesis of Ligand

DOI: 10.37200/IJPR/V24I4/PR2020446
Received: 12 Mar 2020 | Revised: 25 Mar 2020 | Accepted: 10 Apr 2020

Preparation of Solid Ligand Complexes

The solid complexes of the aqueous ligand were prepared from the dissolution of (0.001 ml), (0.404gm) ligand in ethyl alcohol. The ions of the metal complexes were added to each of the (CoCl2.6H2O=0.237gm), (NiCl2.6H2O =0.237 gm), (CuCl2.6H2O=0.17), (ZnCl2=0.136gm), (CdCl2.2H2O=0.228gm) dissolved in distilled water separately forming deposits of solid complexes, nominated recrystallized with absolute ethanol.

Table 1: Shows Some Physical Properties and Percentage of Ligand its Chelating Complexes

Compounds	**Color**	**m.p C̊**	**Yield %**
DPISA ($C_{21}H_{16}N_4O_3S$)	Orange	303-305 C̊	80%
[Co($C_{21}H_{16}N_4O_3S$)$_2$Cl$_2$]	Purple	247-250 C̊	78%
[Ni($C_{21}H_{16}N_4O_3S$)$_2$Cl$_2$]	purple	272-275 C̊	94%
[Cu($C_{21}H_{16}N_4O_3S$)$_2$Cl$_2$]	Dark brown	243-245 decom	89%
[Zn($C_{21}H_{16}N_4O_3S$)$_2$Cl$_2$]	Red	267-270 decom	94%
[Cd($C_{21}H_{16}N_4O_3S$)$_2$Cl$_2$]	Reddish brown	278-280 C̊	79%

III. RESULTS AND DISCUSSION

Mass Spectrum

The mass spectrometry of ligand was studied by this technique. It showed mass fragmentation of the azo- bridge group based on the loss of the nitrogen molecule and the association of the imidazole ring to the rest of the molecule and its continued fragmentation as stated in the literature (8). The mass spectrum of the aforementioned ligand also showed the imidazole fraction (m+/z) at (221) (9). Figure (1) showed the ligand mass spectrometry and the proposed mass fragmentation paths.

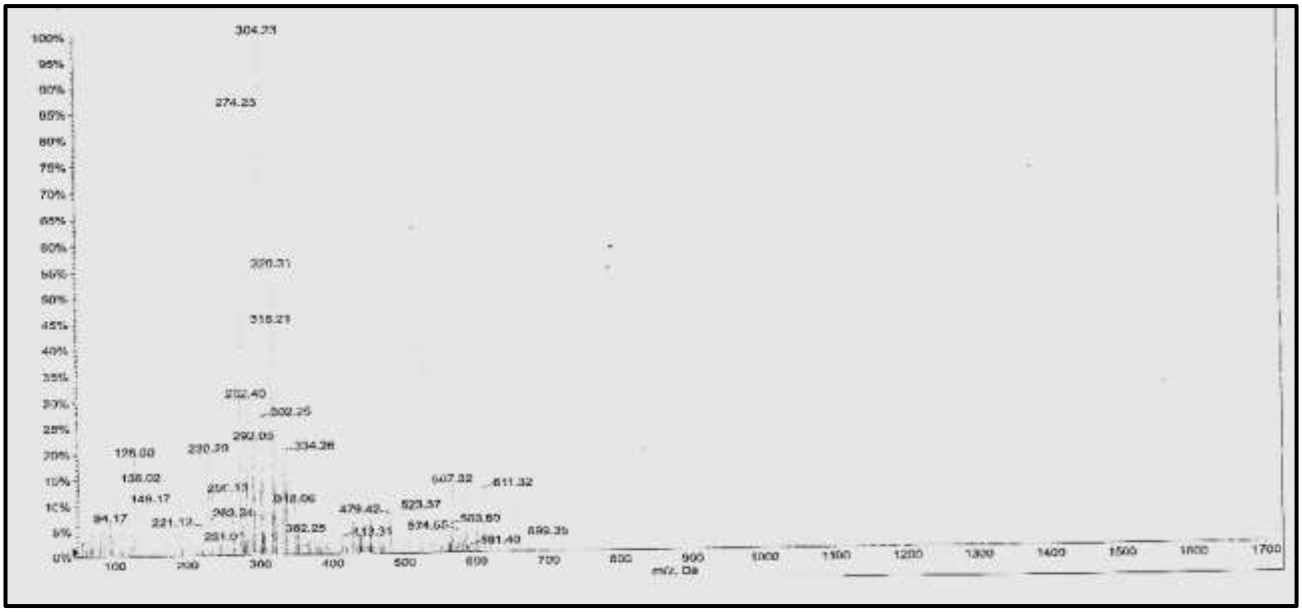


Fig. 1: Mass Spectrum of Ligand

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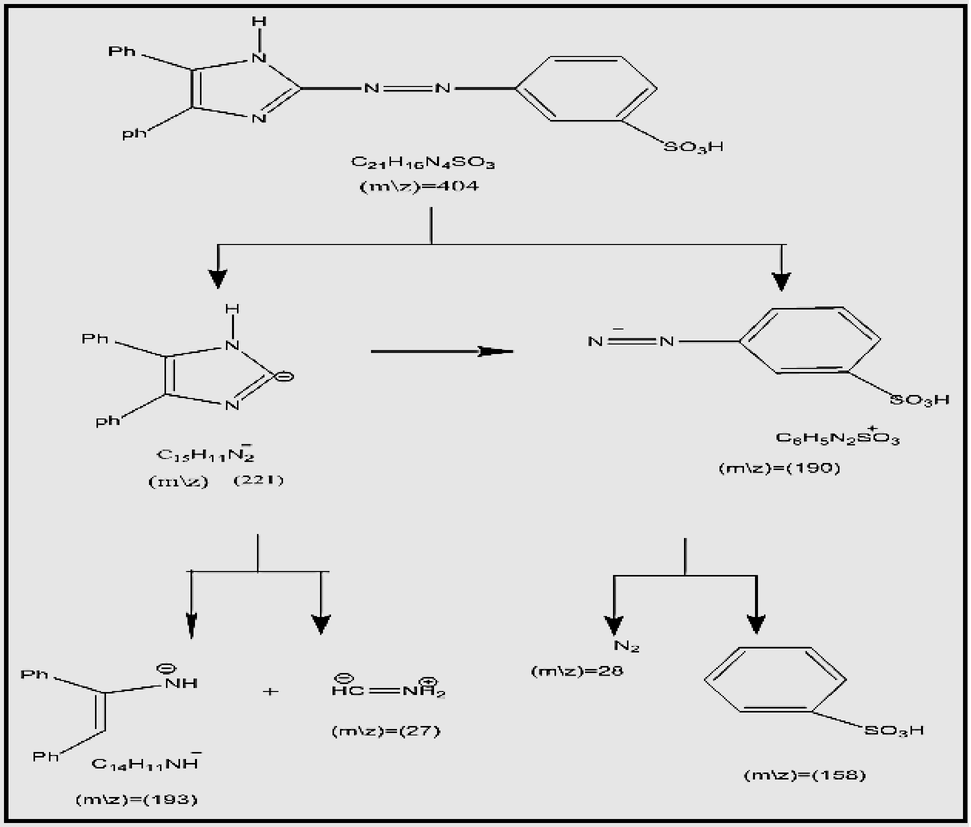

Scheme 2: Segment Fractionation of the Ligand

Nuclear Magnetic Resonance Spectrum (HNMR)

The nuclear resonance spectrum in the DMSO solvent showed multiple signals within the range (6-8) ppm dating back to aromatic ring proton (10-13). The spectrum showed a signal at (2.5) ppm returning to the solvent methyl proton group (14,15). The spectrum also showed a single signal for the proton group of sulfonyl hydroxyl at a displacement of (4.9) ppm.

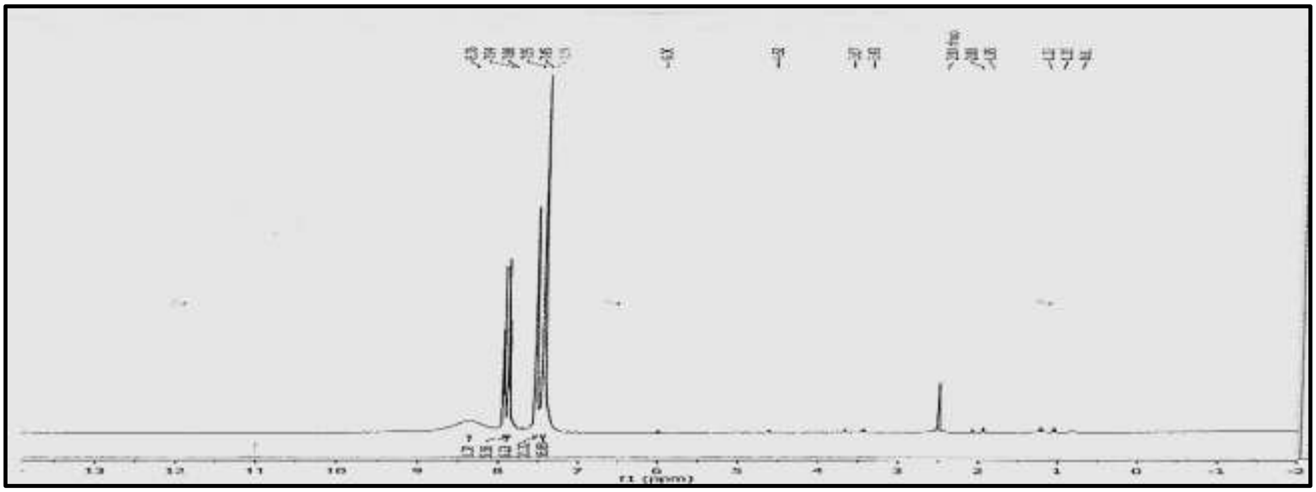

Fig. 2: HNMR Spectra of Ligand

Molar Conductivity

From the results obtained it is clear from the measurement of molar conductivity of the complexes solutions of the ions studied by ligand at concentration (1M) for each complexes and at laboratory temperature using DMSO solvent ranging from (7.73-16.31s.cm2.mol-1) and listed in table (2) there is nonionic characterization of all these complexes. It is consistent with the literature (16) of the complexes of metal ions free of ionic character.

Magnetic Susceptibility

The magnetic susceptibility of Co(II), Ni(II) and Cu(II) complexes was measured and the results show that all magnetic moment values correspond to the values of octahedral complexes high twisting (17,18). The Zn(II) and Cd(II) complex is characterized by its magnetic properties of Diya to its full electronic envelope (d10) (19,20).

Table 2: Molar Conductivity and Magnetic Susceptibility Data of the Complexes

Compounds	**μ_{eff} (BM)**	**Molar conductivity ($s\ cm^2\ mol^{-1}$)**
$[Co(C_{21}H_{16}N_4O_3S)_2Cl_2]$	4.06	10.60
$[Ni(C_{21}H_{16}N_4O_3S)_2Cl_2]$	3.2	12.54
$[Cu(C_{21}H_{16}N_4O_3S)_2Cl_2]$	1.73	7.73
$[Zn(C_{21}H_{16}N_4O_3S)_2Cl_2]$	Diamagnetic	13.53
$[Cd(C_{21}H_{16}N_4O_3S)_2Cl_2]$	Diamagnetic	16.31

Electronic Spectrum

One of the most important and used methods in coordinated chemistry is the ultraviolet- visible spectra through which the effect of consistency has been studied on the quality of the electronic transitions shown in the spectra of the metal complexes and compared with the spectra of free ligand.

The ligand spectrum that was prepared and dissolved in ethanol showed three beams, the first at (287nm) which was diagnosed to move (π→π*) for the heterocyclic imidazole molecule. The second beam wavelength (303nm) is due to the electron transfer (n→π*) of the benzene ring associated with the imidazole ring via the azo- bridge group. (21-24) The third band at (424nm) represents the transfer of the internal charge of ligand towards the heterocyclic imidazole red shift has experienced longer wavelengths this in the spectrum of metal complexes (25-28). The Co(II) complex peaks at (229,337,510) nm due to the transfers (π→π*), (n→π*), (4T1g(4F) → 4T1g(P)) respectively. This gives him the octahedral shape (29,30). The Ni(II)complex spectrum showed three peak, the first at (228nm) going back to any transition (π→π*), the second at (336) nm returning to the (3A2g (F)→3T1g (P)) the third at (5o3nm) attributed to the transition (3A2g(F)→3T2g(F)). this corresponds to octahedral coordination (31,32). The Cu(II) complex spectrum also showed two bands, the first at (210nm) return back to the (π→π*) transition and second at (511nm) attributed to the (2Eg→2T2g(D)). This corresponds to the octahedral shape of the copper complex (33,34). The electronic spectra of Zn(II) and Cd(II) complexes with in ligand does not have any type (d-d) electronic transitions due to the fullness of five (d) orbitals. The consistency between the ligand and the metal ion was evidenced by changes in the intensity of the absorption bands and the emergence of new packages did not exist in the ligand. These are attributed to the charge transfer (C.T) (M →L) (35). Table (4) shows the electronic transitions of ligand and his metal complexes.

Table 3: Shows the Electronic Transitions of Ligand and his Metal Complexes

Compounds	**λ_{max} (nm)**	**Wavenumber (cm^{-1})**	**Transitions**	**Geometry**
L=(DPISA)	287 303 424	34843 33003 23584	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ Charge transfer	-----
$[Co(C_{21}H_{16}N_4O_3S)_2Cl_2]$	299 337 510	33444 29673 19607	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ ${}^4T_1g_{(4F)}\rightarrow {}^4T_1g_{(P)}$	Octahedral
$[Ni(C_{21}H_{16}N_4O_3S)_2Cl_2]$	228 336 503	43859 29761 19880	$\pi\rightarrow\pi^*$ ${}^3A_2g_{(F)}\rightarrow {}^3T_1g_{(P)}$ ${}^3A_2g_{(F)}\rightarrow {}^3T_2g_{(F)}$	Octahedral
$[Cu(C_{21}H_{16}N_4O_3S)_2Cl_2]$	210 511	47619 19569	$\pi\rightarrow\pi^*$ ${}^2Eg\rightarrow {}^2T_2g_{(D)}$	Octahedral
$[Zn(C_{21}H_{16}N_4O_3S)_2Cl_2]$	512	19531	Charge transfer	Octahedral
$[Cd(C_{21}H_{16}N_4O_3S)_2Cl_2]$	509	19646	Charge transfer	Octahedral

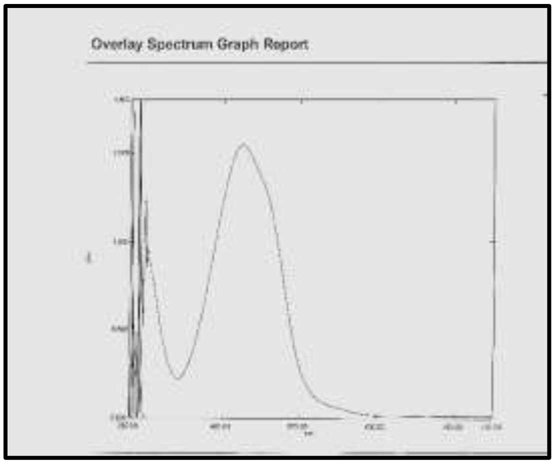

Fig. 3: UV-Vis Spectra of Ligand

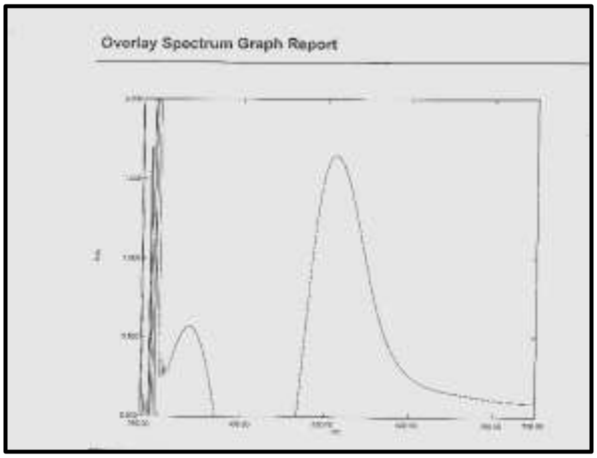

Fig. 4: UV-Vis Spectra of Co (II)

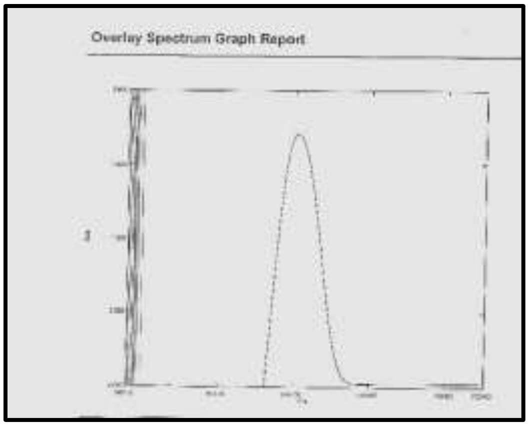

Fig. 5: UV-Vis Spectra of Ni (II)

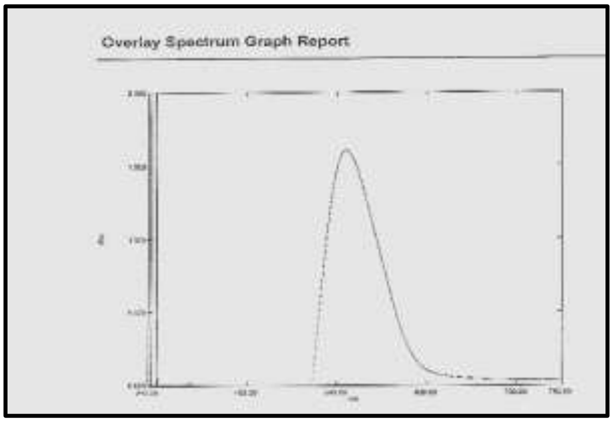

Fig. 6: UV-Vis Spectra of Cu (II)

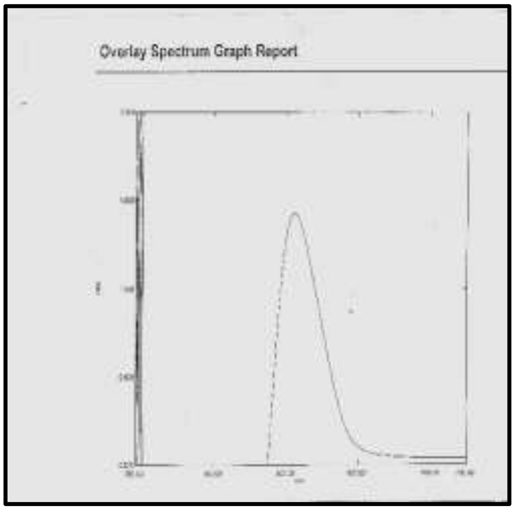

Fig. 7: UV-Vis Spectra of Zn (II)

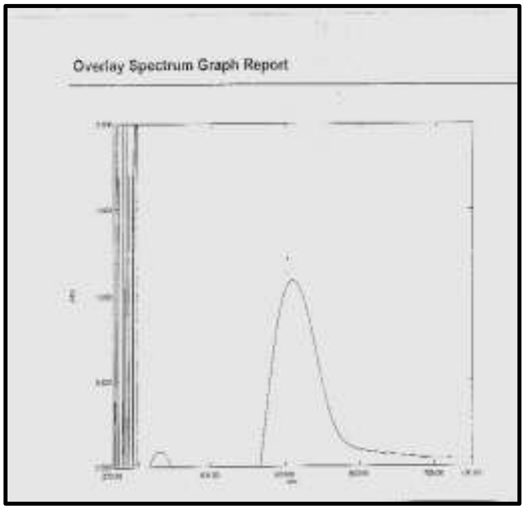

Fig. 8: UV-Vis Spectra of Cd (II)

FTIR Spectrum

One of the primary diagnostic methods used in coordination chemistry is infrared spectra. The absorption packages identify the active groups through which they show consistency between the ligand and the metal ion. (36) The spectrum showed frequencies at site (3062) cm-1 dating back to ν(NH) in the heterocyclic imidazole ring. There were no changes in the spectrum of the metal complexes because they did not participate in the coordination process.

The ν(C=N) group of the heterogeneous imidazole ring showed an absorption frequency at (1558) cm-1. It showed significant changes in the spectra of the complexes due to their coordination (37). The ν (N=N) back of the ligand gantry azo group appeared at site (1473) cm-1 this back experienced significant changes in the spectra of the metal complexes due to the occurrence of the coordination process(38).

The spectrum of ligand also showed a strong beam at frequency (3419) cm-1 due to the insist ν (O-H) group sulfonic. There were no changes in the spectra of the metal complexes because they don't share the coordination. The spectrum of metallic complexes also showed new absorption packages dating back to ν(M-N) (39) at (449-495) cm-1.

Table 4: Shows the Location of the Active Ligand Groups and their Metal Complexes

Compounds	ν(O-H)	ν(N-H) imidazole	ν(C=N) imidazole	ν(N=N) azo	ν(M-N)
L=(DPISA)	3419	3062	1558	1473	-----
$[Co(C_{21}H_{16}N_4O_3S)_2Cl_2]$	3419	3203	1550	1402	449
$[Ni(C_{21}H_{16}N_4O_3S)_2Cl_2]$	3417	3385	1548	1408	453
$[Cu(C_{21}H_{16}N_4O_3S)_2Cl_2]$	3446	3228	1508	1406	495
$[Zn(C_{21}H_{16}N_4O_3S)_2Cl_2]$	3446	3304	1514	1444	460
$[Cd(C_{21}H_{16}N_4O_3S)_2Cl_2]$	3454	3325	1560	1413	474

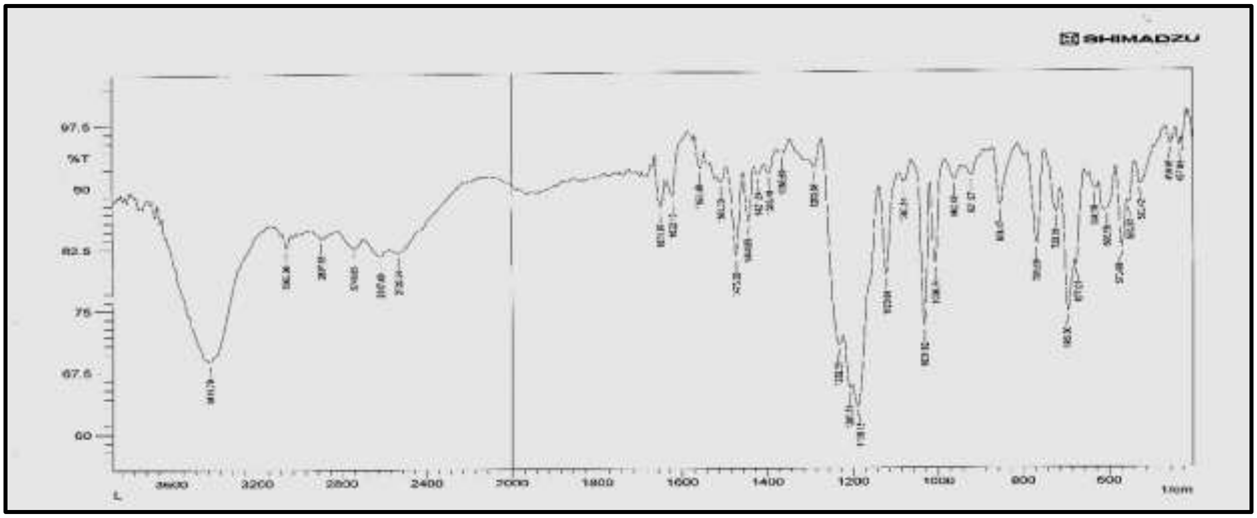

Fig. 9: IR-Spectra of the Ligand

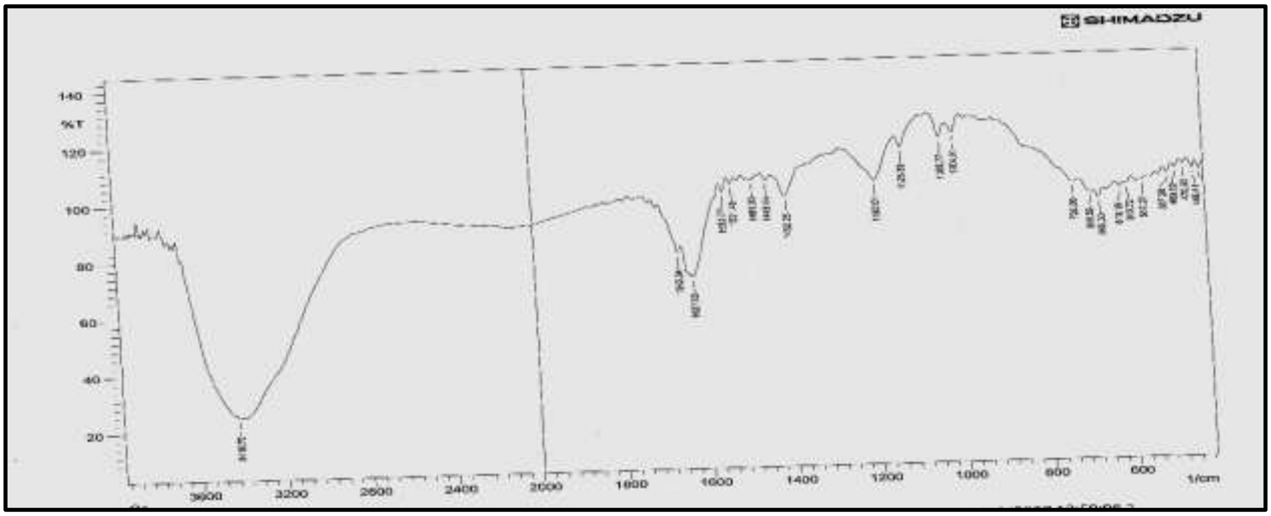

Fig. 10: IR-Spectra of Co (II) Complex with Ligand

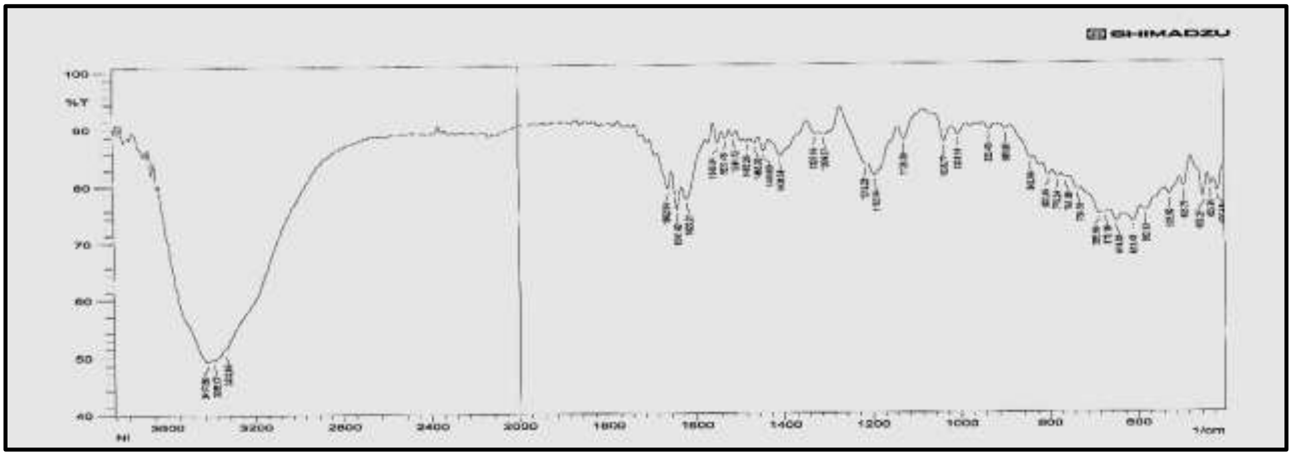

Fig. 11: IR-Spectra of Ni (II) Complex with Ligand

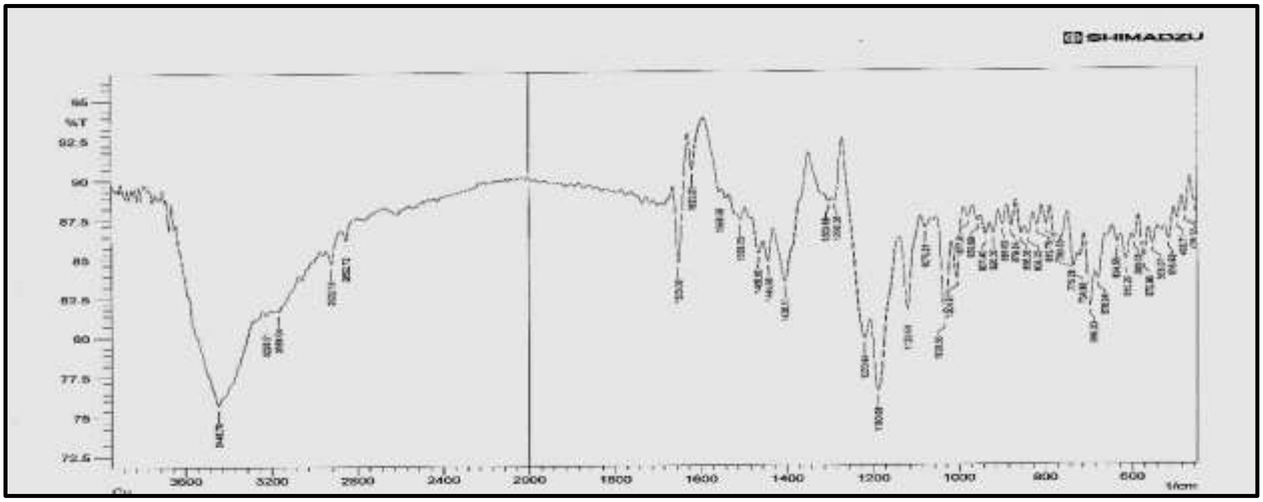

Fig. 12: IR-Spectra of Cu (II) Complex with Ligand

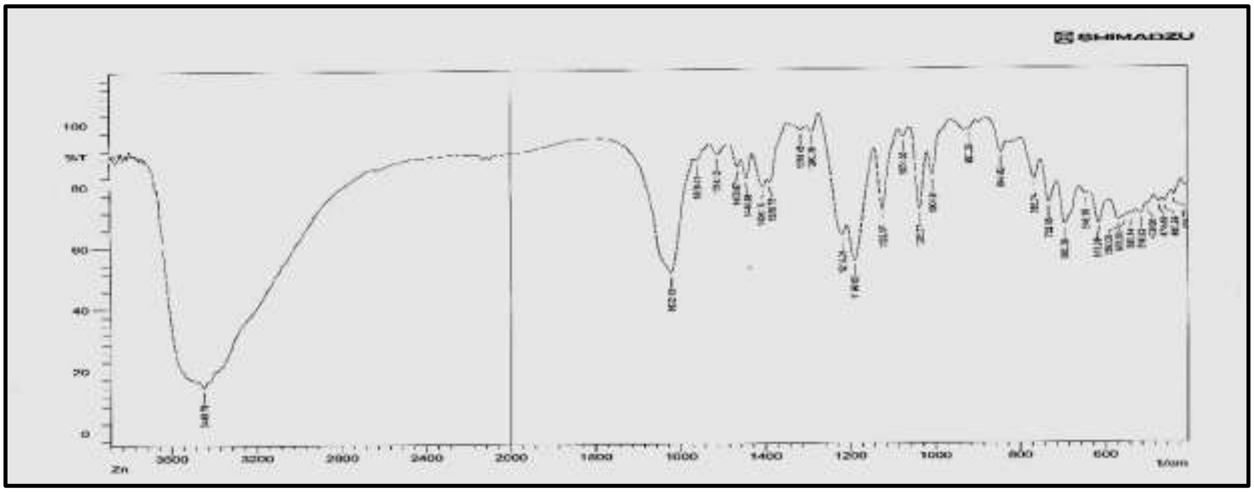

Fig. 13: IR-Spectra of Zn (II) Complex with Ligand

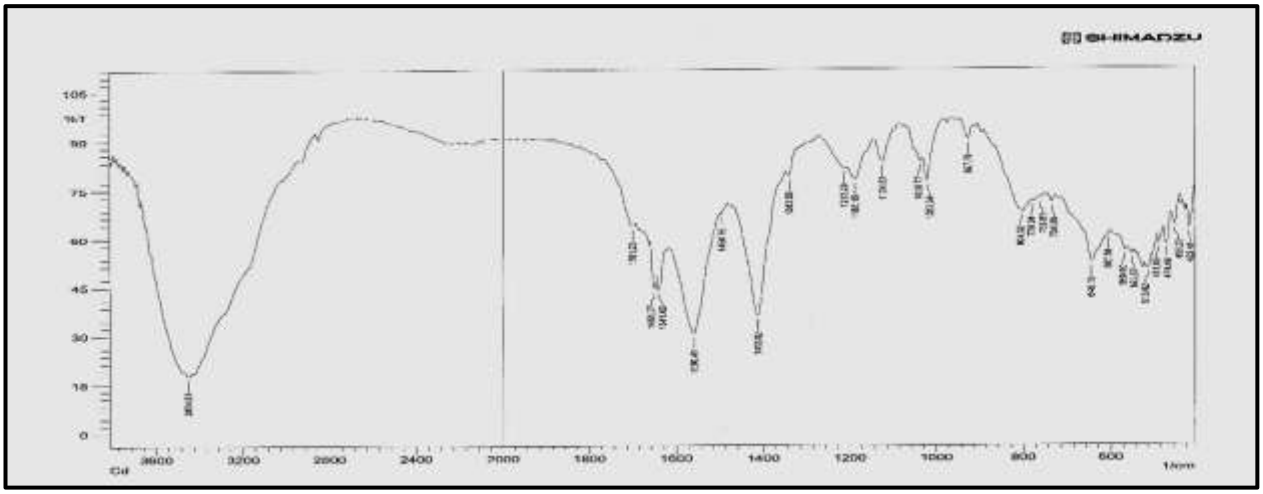

Fig. 14: IR-Spectra of Cd (II) Complex with Ligand

Space Shape

From the results reached it is possible to propose the octahedral from of all metal complexes with ligand (DPISA). The spatial shape of metallic complexes can be illustrated in the following manner.

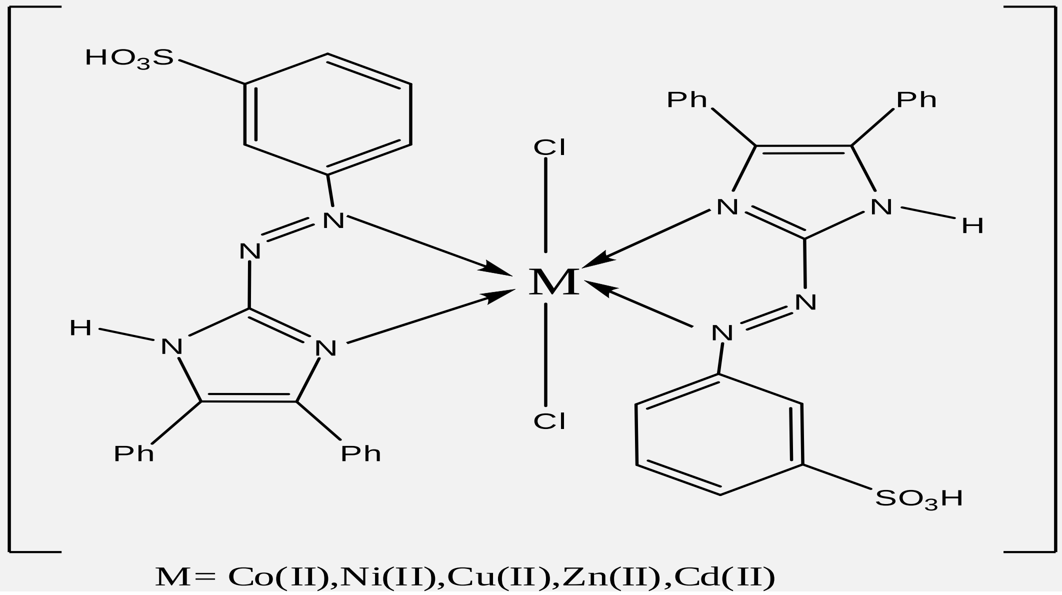

Fig. 15: The Proposed Shape of Complexes with Ligand (PISA)

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DOI: 10.37200/IJPR/V24I4/PR2020446
Received: 12 Mar 2020 | Revised: 25 Mar 2020 | Accepted: 10 Apr 2020

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DOI: 10.37200/IJPR/V24I4/PR2020446
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